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ORIGINAL ARTICLE

Solvent free Cannizzaro reaction applying grindstone technique

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KEYWORDS

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Abstract Cannizzaro reaction of various aryl aldehydes employing solvent free grindstone technique using solid sodium hydroxide was examined and obtained excellent yields (94–99%) with 97–100% conversion rate.

1. Introduction

The redox disproportionation of non-enolizable aldehydes to carboxylic acids and alcohols was conducted in potassium carbonate by Cannizzaro in 1853, known as Cannizzaro reaction (Cannizzaro, 1853; Geissman, 1944; List and Limpricht, 1854; Phonchaiya et al., 2009). The Cannizzaro reaction is one of the oldest and interesting organic reactions that depends on solvent and requires heating in the presence of base, usually concentrated aqueous base. Even though Cannizzaro reaction is the oldest and uses the known reaction method, it continues to attract the attention of chemists due to its interesting synthetic and mechanistic challenges (Abaee et al., 2005; Curini et al., 2005; Vida et al., 2005). The development of the Cannizzaro reaction has been made in the past several years. Strong bases, such as NaOH, KOH, $Ba(OH)_2$ and LiOH (Cannizzaro, 1853; Geissman, 1944; List and Limpricht, 1854; Phonchaiya et al., 2009; Antonio et al., 2008), LiBr with Et_3N (Mojtahedi et al., 2007), cation templates (Vida et al., 2005) with NaOH, solvent-free conditions (Yoshizawa et al., 2001) with KOH at 100 °C, ruthenium-catalyzed transfer hydrogenation (Vida et al., 2005; Kim et al., 2003), in the presence of KOH, NaOH, microwave irradiation (Sharifi et al., 1999; Varma et al., 1998) with $A1_2O_3$(basic), NaOH, and $Ba(OH)_2$, ultrasound mediation (Entezari and Shameli, 2000) in KOH have been introduced for the methodology development of the reaction. Lewis acid (Russell et al., 2000; Yang et al., 2005) catalysts such as, $Cu(OTf)_2$ and $Ln(OH)_3$, Organo-base (Basavaiah et al., 2006), magnesium bromide ethyl etherate and triethylamine in room-temperature (Abaee et al., 2005), aqueous solid–liquid biphasic reaction in presence of cyclodextrins (Canipelle et al., 2011), solid-supported reagents (Reddy et al., 2002) with $KF\text{-}Al_2O_3$, gas-phase process (Sheldon et al., 1997), photo induction (Kagan, 1996) and chiral Lewis acid (Ishihara et al., 2008) have also been applied for the development of the methodology. In addition, crossed Cannizzaro version (Curini et al., 2005) of the reaction with $Yb(OTf)_3$, intramolecular Cannizzaro reaction in the presence of tetraethyl ammonium hydroxide have (Akhigbe et al., 2009) recently been used. Nevertheless, up to this point the development of procedures for the Cannizzaro reaction relied on the

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use of strong base, solvent and hazard workup condition, which led continuing interests to develop an efficient procedure and/or catalyst. We herein describe a simple, efficient, inexpensive, time saving, solvent free procedure for the Cannizzaro reaction applying grindstone technique in the presence of solid sodium hydroxide.

2. Experimental

2.1. General

Melting points were determined on a Fisher–Jones melting-point apparatus and are uncorrected. Infrared spectra were recorded using KBr pellets for solids and neat for liquids on a Perkin–Elmer 1330 grating spectrometer. NMR spectra were obtained using a Bruker-250 spectrometer (250 MHz for ^{1}H NMR and 62.5 MHz for ^{13}C NMR) and 500 MHz Avance Bruker Ultra Shield™ spectrometer and are reported as parts per million (ppm) from the internal standard of tetramethylsilane. Column chromatography was carried out on 60–120-mesh Merck silica gel. Chemicals and solvents were of commercial reagent grade and were used without further purifications.

2.2. General Procedure for the Cannizzaro Reaction

A mixture of aryl aldehyde (**1**, 0.1 mmol) and NaOH (0.1 mmol) was ground together in a mortar using pestle for 10 min. The reaction proceeds exothermically (indicated by rise in temperature of 25–100 °C). The reaction progress was monitored by TLC, after observing no aldehyde presence in the reaction mixture, the whole mass of the reaction mixture was then poured into stirring ice-cold water, neutralized with 2 M HCl and the precipitate formed was filtered, aryl acid was obtained (**2**). The filtrate was then extracted with ethyl acetate, dried over $MgSO_4$, the organic solvent was evaporated, and aryl alcohol was obtained (**3**). Isolated products were characterized by melting points, NMR and mass spectrometric data and were compared with the literature and/or with authentic samples.

2.3. Benzoic acid (*2a*)

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.13 (dd, J = 8.0, 1.3 Hz, 2H), 7.64 (t, J = 7.0 Hz, 2H), 7.50 (t, J = 8.0 Hz, 1H) ppm. ESI-MS (m/z): 121.4 [M-H]$^-$.

2.4. 2-Chlorobenzoic acid (*2b*)

^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.00 (d, J = 8.3 Hz, 1H), 7.48–7.43 (m, 2H), 7.37–7.31 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 170.56, 134.76, 133.60, 132.49, 131.51, 128.33, 126.71 ppm. ESI-MS (m/z): 154.2 (100%) [M (^{35}Cl)-H]$^-$, 156.2 (30%) [M (^{37}Cl)-H]$^-$.

2.5. 2-Fluorobenzoic acid (*2c*)

^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.03 (t, $^3J_{H-H}$ = 7.7 Hz, 1H), 7.58 (q, $^3J_{H-H}$ = 5.0 Hz, 1H), 7.26–7.13 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 169.37, 162.63 (d, $^1J_{C-F}$ = 260.4 Hz), 135.62 (d, $^3J_{C-F}$ = 9.1 Hz), 132.77, 124.11 (d, $^3J_{C-F}$ = 2.25 Hz), 117.46 (d, $^2J_{C-F}$ = 10.25 Hz), 117.17 (d, $^2J_{C-F}$ = 22.12 Hz) ppm. ESI-MS (m/z): 138.7 (100%) [M (^{18}F)-H]$^-$, 139.3 (37%) [M (^{19}F)-H]$^-$.

2.6. 3-Chlorobenzoic acid (*2d*)

^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.07 (s, 1H), 7.98 (d, J = 7.7 Hz, 1H), 7.98 (d, J = 7.7 Hz, 1H), 7.57 (d, J = 8.10 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 170.93, 134.68, 133.89, 130.96, 130.24, 129.83, 128.30 ppm. ESI-MS (m/z): 154.2 (100%) [M (^{35}Cl)-H]$^-$, 155.9 (33%) [M (^{37}Cl)-H]$^-$.

2.7. 3-Methoxybenzoic acid (*2e*)

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.71 (d, J = 7.6 Hz, 1H), 7.61 (s, 1H), 7.36 (t, J = 7.9 Hz, 1H), 7.14 (dd, J = 8.2, 2.5 Hz, 1H), 3.85 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 171.98, 159.54, 130.55, 129.51, 122.66, 120.44, 114.33, 55.43 ppm. ESI-MS (m/z): 150.1 [M-H]$^-$.

2.8. 4-Bromobenzoic acid (*2f*)

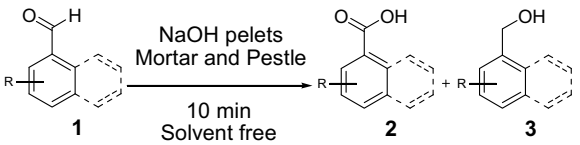
^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.94 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$ + CD_3OD, 62.5 MHz) δ 167.69, 131.21, 130.94, 129.15, 127.49 ppm. ESI-MS (m/z): 198.9 (95%) [M (^{79}Br)-H]$^-$, 199.7 (100%), 200.8 (10%) [M (^{81}Br)-H]$^-$.

2.9. 4-Chlorobenzoic acid (*2g*)

^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.02 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$ + CD_3OD, 62.5 MHz) δ 167.29, 138.62, 130.57, 128.56, 127.95 ppm. ESI-MS (m/z): 154.3 (100%) [M (^{35}Cl)-H]$^-$, 156.1 (40%) [M (^{37}Cl)-H]$^-$.

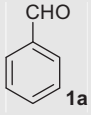
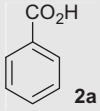
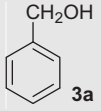
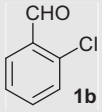
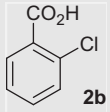
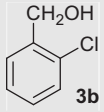
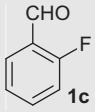
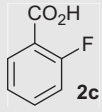
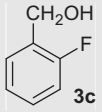
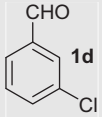
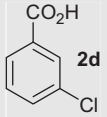
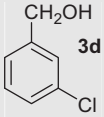
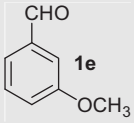
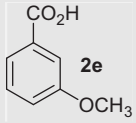
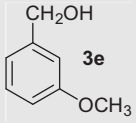
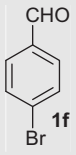
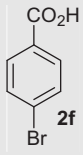
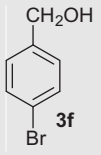
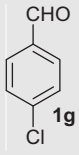
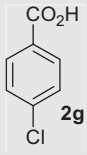
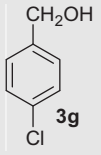
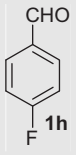
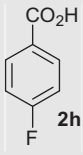
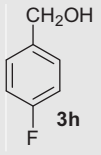
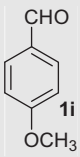
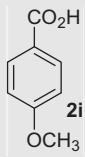
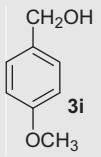
2.10. 4-Fluorobenzoic acid (*2h*)

^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.11 (t, $^3J_{H-H}$ = 7.6 Hz, 2H), 7.13 (d, $^2J_{H-H}$ = 8.3 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 170.91, 166.30 (d, $^1J_{C-F}$ = 253.4 Hz), 132.85 (d, $^3J_{C-F}$ = 9.5 Hz), 125.50 (d, $^4J_{C-F}$ = 3.1 Hz), 115.46 (d, $^2J_{C-F}$ = 22.06 Hz) ppm. ESI-MS (m/z): 138.6 (100%) [M (^{18}F)-H]$^-$, 139.2 (30%) [M (^{19}F)-H]$^-$.



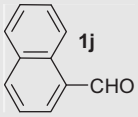
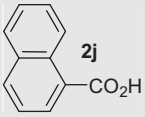
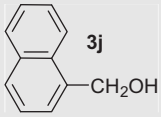
Scheme 1 Cannizzaro reaction of various aryl aldehydes using solid NaOH pellets.

Table 1 Cannizzaro reaction of aryl aldehydes in the presence of NaOH applying grindstone technique.[a]

Entry	Products		Con.[c]/Y[d] (%)	Mp (°C) [Lit. mp (°C)] of acids
	Acid	Alcohol[b]		
			100/96	124[121] Gedye et al. (1988)
			100/98	139[139] Clarke and Taylor (1943)
			100/98	124[122] Wolfgang et al. (2002)
			98 / 96	154[153] Baelen and Maes (2008)
			99/97	105[105] Morimoto and Kakiuchi (2004) and Cacchi et al. (2007)
			98/95	152[152] Yang et al. (2004)
			98/94	242[240] Yang et al. (2004)
			97/95	185[184] Yang et al. (2004)
			98/96	183[179] Wolfgang et al. (2002)

(*continued on next page*)

Table 1 (*continued*)

Entry	Products		Con.[c]/Y[d] (%)	Mp (°C) [Lit. mp (°C)] of acids
	Acid	Alcohol[b]		
 1j	 2j	 3j	100/99	161[159] Gilman et al. (1943)

[a] Aldehyde and solid NaOH (1 equiv.) were ground for approximately 10 min.
[b] Alcohols were not purified except for **3j**.
[c] Conversion of aldehydes.
[d] Isolated yields.

*2.11. 4-Methoxybenzoic acid (**2i**)*

^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.05 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 3.86 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 171.53, 164.01, 132.33, 121.58, 113.72, 55.48 ppm. ESI-MS (m/z): 150.4 $[M\text{-}H]^-$.

*2.12. 1-Naphthoic acid (**2j**)*

^{1}H NMR ($CDCl_3$, 250 MHz) δ 9.09 (d, J = 8.5 Hz, 1H), 8.41 (d, J = 7.1 Hz, 1H), 8.09 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 7.3 Hz, 1H), 7.54 (d, J = 7.9 Hz, 2H), ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 173.22, 134.64, 133.89, 131.84, 131.59, 128.70 128.10, 126.31, 125.88, 125.56, 124.52 ppm. ESI-MS (m/z): 170.7 $[M\text{-}H]^-$.

*2.13. 1-Naphthoic ethanol (**3j**)*

Mp. 60–61 °C (Lit[26] 61.5–62 °C) ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.11 (d, J = 7.7 Hz, 1H), 7.86 (dd, J = 6.3, 2.1 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.57–7.40 (m, 4H), 5.14 (d, J = 5.7 Hz, 2H), 1.74 (t, J = 5.9 Hz, 1H, –OH), ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 136.09, 133.56, 131.00, 128.48, 128.27, 126.12, 125.68, 125.25, 125.06, 123.48, 63.12 ppm. ESI-MS (m/z): 141.6 $[(M\text{-}OH)+H]^+$.

3. Results and discussion

In this communication, we have disclosed the conversation of aryl aldehydes (**1**) to aryl carboxylic acid (**2**) and aryl alcohol (**3**). Reaction proceeds without any solvents and grindstone technique was used for the redox disproportion of various aryl aldehydes (**1**) in the presence of sodium hydroxide pellets (Scheme 1).

While a mixture of aryl aldehyde (**1**) and one equivalent of solid NaOH plates were ground for approximately 10 min. and under the hood, the reaction proceeds exothermically (indicated by rise in temperature of 25–100 °C), the whole mass was then poured into ice cold water, acidified with 2 M HCl and solid precipitate was collected as analytical pure aryl acid. Extraction of water portion with organic solvent gave aryl alcohol, herein, we have shown the data only for the isolation of acid and it is summarized in Table 1.

However, for 1-Naphthanaldehyde, we have isolated the 1-Naphthoic ethanol (**3j**) (Ragnarsson et al., 2002) as well as 1-Naphthoic acid (**2j**). The procedure does not employ any halogenated solvents, additional additives, and/or catalysts, which are important from the economical and environmental point of view. In addition, formation of side products that are normally observed under other conditions was not detected. For all the aldehydes used, the conversion rate was almost 100% (no aldehyde was present based on TLC development and NMR experiment). It should be noted that halogen/methoxy substituted at 4-position of aldehydes gives lower yields.

4. Conclusion

In conclusion, a simple and efficient procedure for the Cannizzaro reaction was established. This present method is superior since it is eco-friendly, advantageous over previously described methods in yield, requires no special apparatus, there is simplicity of operation, and is non-hazardous, simple and convenient.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.arabjc.2012.02.010.

References

Abaee, M.S., Sharifi, R., Mojtahedi, M.M., 2005. Org. Lett. 7, 5893–5895.
Akhigbe, F., Ryppa, C., Zeller, M., Brückner, C., 2009. J. Org. Chem. 74, 4927–4933.
Antonio, J.R.-S., Yolanda, V., Rafael, S., Ezequiel, P.-I., 2008. Tetrahedron 64, 11661–11665.
Baelen, G.V., Maes, B.U.W., 2008. Tetrahedron 64, 5604–5619.
Basavaiah, D., Sharada, D.S., Veerendhar, A., 2006. Tetrahedron Lett. 47, 5771–5774.
Cacchi, S., Cotet, C., Fabrizi, G., Forte, G., Goggiamani, A., Martin, M., Martin, E., Molins, E., Moreno-Manaús, M., Petrucci, F., Roig, A., Vallriberad, A., 2007. Tetrahedron 63, 2519–2523.

Canipelle, M., Landy, D., Fourmentin, S., 2011. J. Incl. Phenom. Macrocycl. Chem. 69, 349–353.
Cannizzaro, S., 1853. Justus Liebigs Ann. Chem. 88, 129–130.
Clarke, H.T., Taylor, E.R., 1943. Org. Synth. 2, 135.
Curini, M., Epifano, F., Genovese, S., Marcotullio, M.C., Rosati, O., 2005. Org. Lett. 7, 1331–1333.
Entezari, M.H., Shameli, A.A., 2000. Ultrason. Sonochem. 7, 169–172.
Gedye, R.N., Smith, F.E., Wsestaway, K.C., 1988. Can. J. Chem. 66, 17–26.
Geissman, T.A., 1944. Org. React. 2, 94–113.
Gilman, H., St John, N.B., Schulze, F., 1943. Org. Synth. 2, 425.
Ishihara, K., Yano, T., Fushimi, M., 2008. J. Fluorine Chem. 129, 994–997.
Kagan, J., 1996. Tetrahedron Lett. 7, 6097–6102.
Kim, B.T., Cho, C.S., Kim, T.J., Shim, S.C., 2003. J. Chem. Res., 368–369.
List, K., Limpricht, H., 1854. Ann. 90, 190–210.
Mojtahedi, M.M., Akbarzadeh, E., Sharifi, R., Abaee, M.S., 2007. Org. Lett. 9, 2791–2793.
Morimoto, T., Kakiuchi, K., 2004. Angew. Chem., Int. Ed. 43, 5580–5588.
Phonchaiya, S., Panijpan, B., Rajviroongit, S., Wright, T., Blanchfield, J.T., 2009. J. Chem. Educ. 86, 85–86.
Ragnarsson, U., Grehn, L., Maia, H.L.S., Monteiro, L.S., 2002. J. Chem. Soc. Perkin Trans. 1, 97–101.
Reddy, B.V.S., Srinivas, R., Yadav, J.S., Ramalingam, T., 2002. Synth. Commun. 32, 219–223.
Russell, A.E., Miller, S.P., Morken, J.P., 2000. J. Org. Chem. 65, 8381–8383.
Sharifi, A., Mojtahedi, M.M., Saidi, M.R., 1999. Tetrahedron Lett. 40, 1179–1180.
Sheldon, J.C., Bowie, J.H., Dua, S., Smith, J.D., O'Hair, R.A., 1997. J. Org. Chem. 62, 3931–3937.
Varma, R.S., Naicker, K.P., Liesen, P.J., 1998. Tetrahedron Lett. 39, 8437–8440.
Vida, Y., Perez-Inestrosa, E., Suau, R., 2005. Tetrahedron Lett. 46, 1575–1577.
Wolfgang, M., Adriano, F.I., Matthias, B., 2002. J. Organomet. Chem. 641, 30–40.